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REPORTS
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R.J.

FINAL REPORT FOR RESEARCH AGREEMENT
INT-96079-RJVA
"Analysis of the Atmospheric Influence of Trace Gas Emission from Biomass Fires using New Technology"
UNIVERSITY OF MONTANA
FS Contact: Dr. Ronald A. Susott
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Final Report: INT96079-RJVA

To:
USDA Forest Service
Rocky Mountain Research Station
Intermountain Fire Sciences Laboratory
Missoula, MT 59807

By:

Robert J. Yokelson
Associate Research Professor, Department of Chemistry, University of Montana

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Geoffrey N. Richards
Professor Emeritus, Department of Chemistry, University of Montana

April 1, 1998

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Executive Summary

Rationale for and scope of work. Biomass burning can have a strong influence on local-global atmospheric chemistry, but characterization of this influence is complicated by the complex, rapidly-changing, and difficult-to-measure composition of both smoke and "clean air." We have shown that open-path, in-situ, Fourier transform infrared (FTIR) spectroscopy is well-suited for continuous, interference-free, measurement of a broad range of reactive and stable gases and can contribute significantly to our knowledge of atmospheric (or smoke) composition. This is especially useful for those reactive gases which are difficult to measure by other methods. In this report we emphasize four major activities:

1. Simultaneous measurements of both reactive and stable emissions from biomass fires which allow us to estimate the *relative* importance and influences of the reactive gases, such as heavy hydrocarbons and oxygenated organic compounds, in atmospheric chemistry and to firefighter health.
2. Characterizing the sensitivity and accuracy of our new open-path optical technique by the preferred method: i.e. detailed intercomparison (where possible) with more established instrumentation.
3. Determining the feasibility of using the FTIR in the field for same-day analysis of stainless steel canisters. This could eliminate the delay time (often months) currently preceding gas chromatographic canister analysis and could also reduce the need for a large inventory of canisters (currently 400 cans at a cost of $160,000) if a field can-cleaning system was also deployed.
4. Assessing the implications of our smoke composition data in light of the potential health risks faced by firefighters and presenting "user-friendly" summaries of our findings at the Forest Service/NWCG National Health Hazards of Smoke Conference in Missoula in April of 1997. Participating in discussions relative to the need for, and design of, protective equipment or other mitigation strategies.

Organization of this report. In Part 1 each objective of RJVA96079 is listed and progress to date in addressing that objective is summarized. In Parts 2 and 3, we append brief excerpts from preliminary drafts of upcoming publications which contain more details relevant to the objectives.

1. Summary of Accomplishments on the Research Objectives of RJVA96079.

A. Quantify a broad range of reactive and stable fire emissions using open-path FTIR spectroscopy deployed above well-characterized "full-scale" fires in *grass and hardwood* fuels at the Intermountain Fire Sciences Laboratory (IFSL).

A.1. New information on fire emissions. Our research has quantified many of the gases measured in traditional combustion research and simultaneously quantified two major new types of reactive gases in the initial emissions from fires. These new types of gases are, primarily, oxygenated organic compounds (OVOC) and monoterpenes. The emissions of oxygenated organics from smoldering combustion in both grass and hardwood fuels, were published in: **R. J. Yokelson, D. E. Ward, R. A. Susott, J. Reardon, and D. W. T. Griffith, Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, *J. Geophys. Res.* 102, 18865 (1997).** The emissions of OVOC from full-scale, well-characterized fires in the hardwood fuels, poplar and sagebrush, were also previously published in **R. J. Yokelson, D. W. T. Griffith, R. A. Susott, and D. E. Ward, Spectroscopic Studies of Biomass Fire Emissions, in *International Perspectives on Landscape Fires,* edited by J. Greenlee, in press, International Assoc. of Wildland Fire, Fairfield, WA., (1997).** Copies of both of these publications were attached to a previous final report: **R. J. Yokelson and G. N. Richards, Analysis of Trace Gases Using Optical Remote Sensing, *Final Report: INT95009-RJVA,* USDA Forest Service Rocky Mountain Research Station, February 10, 1998.** The emissions of OVOC from full-scale, well-characterized grass fires were measured in joint experiment with NASA in October 1996. The analysis of these fires is nearing completion and the results are being prepared for publication by Dr. Jon Goode (supported by our NSF funding). Selected preliminary results from an early draft of this paper are attached as Part 2 of this report.

Estimating smoke concentration of terpenes has had three major parts:

1. Measurement of IR absorption intensity by accurately known amounts of each common monoterpene which I carried out in collaboration with Dr. James Burkholder of the NOAA Aeronomy Laboratory.
2. The development of new spectral analysis techniques to estimate the terpene signal in smoke spectra carried out in collaboration with Dr. David Griffith of the University of Wollongong (supported by our NSF funding).
3. Attempting independent verification of our FTIR terpene results by other methods. This has been unsuccessful so far and may be due to losses during sample storage.

Recently, however, a group in France has reported the presence of high levels of a terpene in a laboratory fire in juniper fuels.

Some of our terpene-related activities are described in selected excerpts from a preliminary draft of an upcoming publication which is attached as Part 3 of this report. In summary the new FTIR has now been used on > 100 fires to quantify numerous gases including carbon dioxide, carbon monoxide, methane, ethane, ethene, ethyne, propene, limonene, β-pinene, Δ^3-carene, formaldehyde, 2-hydroxyethanal, methanol, phenol, acetic acid, formic acid, nitric oxide, nitrogen dioxide, ammonia, hydrogen cyanide, sulfur dioxide, and carbonyl sulfide.

A.2. Atmospheric implications of the new smoke composition information. In summary, terpenes could strongly effect smoke chemistry through their fast reactions with OH, NO_3, and O_3 and the oxygenated organic compounds represent an important source of HO_2 and OH in the plume which will act to destroy other pollutants. These influences are developed in more detail below.

Primary and secondary products. Hydrocarbons, carbon monoxide (CO), and nitric oxide (NO) are examples of gases which appear in the atmosphere largely due to direct emission by human or "natural sources" and are often referred to as "primary products." In general terms, primary products are transformed into "secondary products" by the action of sunlight and "oxidants." To illustrate, several important NO_2 sources are shown in reactions 1a-1c. (The classification as a primary or secondary product is general; for example, NO_2 sources include soils and lightning.)

(1a)	NO	+	O_3	→	NO_2	+	O_2	
(1b)	NO	+	HO_2	→	NO_2	+	OH	
(1c)	HNO_3	+	uv light	→	NO_2	+	OH	

Ozone formation. The most studied secondary product in the atmosphere is ozone (O_3) because of its importance as an air toxic, greenhouse gas, oxidant, and a source of other oxidants. In remote marine atmospheres the O_3 concentration is mainly controlled by the following reactions comprising the "photostationary state".

(2)	NO_2	+	uv light	→	NO	+	O	
(3)	O	+	O_2	→	O_3			(fast)
(4)	NO	+	O_3	→	NO_2	+	O_2	(slow)

The photostationary state can be perturbed by primary products such as NO, CO, or hydrocarbons. For example, methyl nitrate formation (from methane) prevents some O_3 destruction by NO and leads to later release of the O_3 precursor NO_2 as shown below.

(5)	CH_4	+	OH	→	H_2O	+	CH_3
(6)	CH_3	+	O_2	→	CH_3O_2		
(7)	CH_3O_2	+	NO	→	CH_3ONO_2		(methyl nitrate)
(8)	CH_3ONO_2	+	heat	→	CH_3O	+	NO_2

The oxidation of CO is a major source of tropospheric O_3 as follows.

(9)	CO	+	OH		→	CO_2	+	H	
(10)	H	+	O_2		→	HO_2			
(11)	HO_2	+	NO		→	OH	+	NO_2	
(12)	NO_2	+	uv light		→	NO	+	O	
(13)	O	+	O_2		→	O_3			
(14)	CO	+	uv	+ $2O_2$	→	CO_2	+	O_3	(net)

Oxidant formation and oxidizing capacity. The three main molecules which drive chemical change in the atmosphere (including pollutant destruction) are OH, O_3, and NO_3. Many other species are important oxidants (such as HO_2, NO_2, and SO_2). However, the concentration of the three main oxidants (especially OH) largely controls the "oxidizing capacity" of the atmosphere; i.e. its ability to clean itself. The main source of OH is usually photolysis of a very small fraction of the O_3 as follows.

(15)	O_3	+	uv	→	O_2	+	$O(^1D)$
(16)	$O(^1D)$	+	H_2O	→	2OH		

The main source of NO_3 is reaction (17).

(17)	NO_2	+	O_3	→	NO_3	+	O_2

Thus O_3 has some good effects because it is an oxidant of other pollutants and a source of OH and NO_3.

The possible atmospheric influence of high levels of oxygenated organic molecules in smoke plumes. As mentioned above, the OP-FTIR work has led to the conclusion that many oxygenated organics (formaldehyde, methanol, acetic acid, phenol, formic acid, etc.) are present in fresh biomass burning plumes at levels much higher than previously thought and at levels much higher than in fresh plumes from fossil fuel combustion. This enhancement is probably due mainly to pyrolysis of biomass (which is about 50% oxygen unlike fossil fuel). Many of these oxygenated compounds react in the atmosphere to form formaldehyde. An important fate of formaldehyde in the atmosphere is as follows.

(18)	H_2CO	+	uv	→	HCO	+	H
(19)	H	+	O_2	→	HO_2		
(20)	HCO	+	O_2	→	HO_2	+	CO

In an initial fire plume, H_2CO is ~ 2% of CO so the extra CO from this source would be expected to contribute negligible additional O_3. However HO_2 will likely undergo reaction (21) and therefore represents an important additional source of OH (primarily desired atmospheric constituent) which does not require an O_3 (primarily undesired) precursor.

(21)	HO_2	+	NO	→	NO_2	+	OH

Atmospheric chemistry model output. Due to the many competing influences in any atmospheric system, the chemistry of a biomass-fire smoke-plume injected into the atmosphere was explored by our collaborators Sherri Mason and Dr. Richard Field using a photochemical model developed at NCAR. Some tentative, preliminary results are discussed next.

Initial NO (NO_o) is usually about 2% of initial CO (CO_o) in a fire plume and this ratio can vary from about 1 to > 5 %. In a prognostic model application this initial ratio was varied from 1 to 6 %. Increasing the NO_o/CO_o ratio by a factor of six caused an (expected) increase in both O_3 and OH production by a factor of 2.8. (Since NO is a flaming product and CO is a smoldering product; high CE fires may have a higher O_3 formation potential.) In another test, shown in Figure 1, NO_o was fixed at 2% of CO_o and H_2CO_o was varied from 0 to 4 % of CO_o. Increasing H_2CO_o/CO_o from 0 to just 2 % (an average observed value in fresh fire plumes) caused only a 1.3% increase in O_3 production. However, this also caused a 16% increase in HO_2 and a 6 % increase in OH. The combined effect of all the oxygenated organics could be several times larger. Thus it is worthwhile to explore whether a biomass fire plume may have a higher internal oxidizing capacity than industrial combustion plumes.

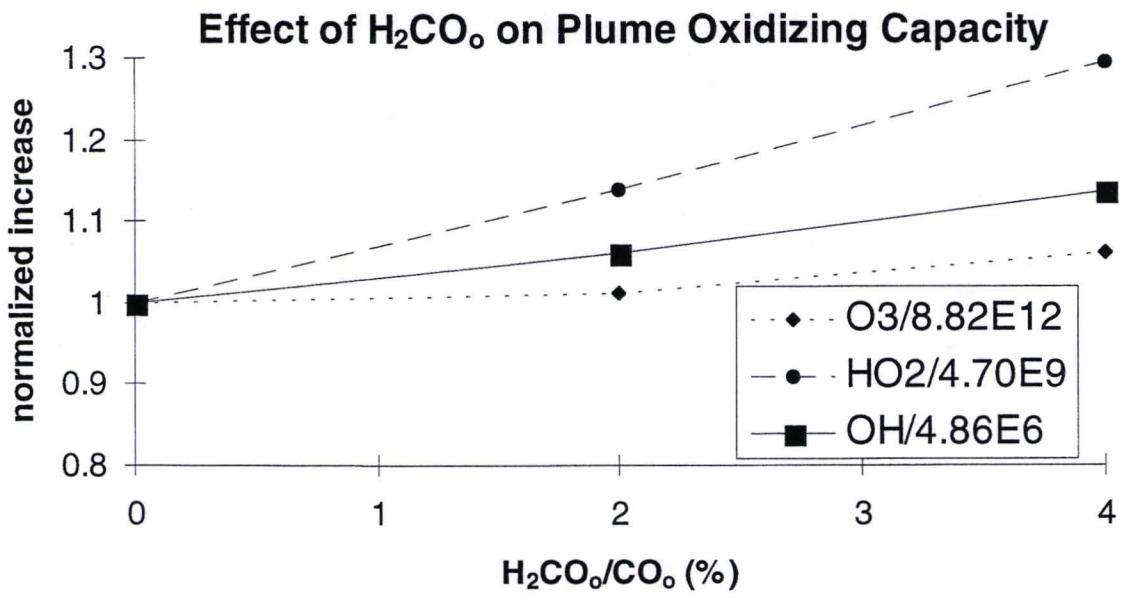

Figure 1. Preliminary model exploration of atmospheric effects of formaldehyde. (See text)

B. Perform an intercomparison of measurements of H_2O, CO_2, CO, and NO_x between laboratory instruments at IFSL and FTIR measurements.

Intercomparison of independent measurement techniques is the best way to determine the actual uncertainty in both a measurement and any scientific conclusions based on the measurement. It is very important to intercompare our FTIR data with conventional (EPA certified) techniques for two other complementary reasons. The EPA certified techniques have a high probability of yielding the correct answer, especially for relatively clean background air, and thus can help us detect problems with our new FTIR technique. Conversely, no EPA techniques have ever been certified for the "dirty" smoke environment where the potential for chemical interference is high. Since FTIR measurements are almost immune to chemical interference they are of use in checking the performance and accuracy of EPA certified techniques in previously untested conditions. The FTIR background and smoke measurements for CO_2, CO, and NO carried out in the IFSL lab in 1989, *before installation of mixing orifice in the stack*, were all within 10% of the simultaneous measurements with existing, conventional (EPA-certified) IFSL instrumentation. This level of agreement between a path-integrated and a point measurement which, in addition, have two different time responses is excellent. These results are detailed in **R. J. Yokelson, D. W. T. Griffith, J. B. Burkholder, and D. E. Ward, Accuracy and Advantages of Synthetic Calibration of Smoke Spectra, in *Optical Remote Sensing for Environmental and Process Monitoring*, pp. 365-376, Air & Waste Manage. Assoc., Pittsburgh, PA., (1996)**.

The new IFSL-FTIR CO_2 background measurements were rigorously intercompared with IFSL Licor model 6262 after installation of the mixing orifice. The FTIR was less than 2% different from the NDIR standard. This is about the stated accuracy of both techniques. These results were described in **R. J. Yokelson, D. E. Ward, R. A. Susott, J. Reardon, and D. W. T. Griffith, Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, *J. Geophys. Res.* 102, 18865 (1997)**. Both publications were attached to the previous final report cited earlier.

A more demanding test of the new IFSL-FTIR was carried out as part of the joint experiment with NASA. In this experiment the FTIR pathlength was shortened in anticipation of large fires. After installation of the FTIR in the stack it was found necessary to build very small fires to avoid saturation of the NASA sensors. Thus, during this experiment, the FTIR, often in operation near its detection limits, made measurements in smoke and background air of H_2O, CO_2, and CO at the same time as IFSL conventional "real-time" instrumentation. The FTIR data was acquired as 10 second averages to increase the S:N. For the real-time instruments there are inherent response times and sample line delays which are much longer than the 1 second readout period. In these comparisons the relative agreement or shape of the temporal profiles was always excellent. The intercomparison for CO is nearing completion and can be seen in Part 2, while the intercomparison for water and CO2 is still in progress.

During the NASA experiment the FTIR measurements were also compared to IFSL-GC/FID measurements of CO_2, CO, CH_4, and C_2H_4 made on canister samples of (ostensibly well-mixed) smoke. This was done by averaging together spectra acquired

during the time the canisters were filled and analyzing the resulting spectra for the molecules listed above. The canister results are believed by Dr. Baker of the IFSL to be accurate to ± 2%. We estimate the FTIR results (at the current level of analysis effort) to be accurate to about ± 5% or the S:N level. (We are currently building a state-of-the-art gas handling system with NSF funds which will allow us (among other things) to push the FTIR accuracy to higher levels.) The current level of agreement between these techniques is usually less than their combined uncertainty as shown in Figure 2 of Part 2.

We have begun comparing FTIR data acquired during plume penetrations by the Forest Service King Air B-90 to canister-GC/FID results from the same penetrations. Due to the airplane velocity and limited plume extent, these experiments had to be carried out in such a way that each sample included a varying amount of background air. Thus the absolute or excess levels are not particularly meaningful or comparable, but it can be shown (simply) that the excess *ratios* (or for example measured MCE) should be identical by any properly working technique if the smoke was well-mixed. The preliminary comparison for the airborne FTIR (AFTIR) and GC/FID MCE is very good in some cases, but, as expected, not as good for low (on the order of the accuracy) CO_2 enhancements. This may be improved simply by analyzing only the AFTIR spectra with peak CO_2 levels rather than averaging all the spectra acquired while in smoke or by finding improved analysis techniques (several are under consideration). Some preliminary intercomparison is shown in Table 1.

In summary, the major benefit of FTIR is to give results for more types of gases, including many which were previously poorly characterized, with an accuracy which is very high compared to most uncertainties in the study of biomass burning.

Table 1. Preliminary intercomparison (CO and CO_2): AFTIR and Cans.

Flight Time (s)	Can from Bag	FTIR MCE	CAN MCE
3123		0.946	0.942
3300	x		0.941
7283		0.920	0.915
7400	x		0.908
7598		0.921	nm
7968		0.930	0.936
8200	x		0.915

C. Develop the engineering considerations needed to couple the FTIR with a system for doing analyses on the stainless steel canister samples.

To date, IFSL stainless steel canisters have been filled during several-month long, remote field experiments and then brought back as a group of 200 or more to the IFSL. Thus, they are usually analyzed several months after collection. This means that the "can data" is not available for feedback on an experiment while the experiment is in progress. Dr. Ward and Dr. Susott of IFSL requested that I investigate the possibility of bringing the FTIR to field locations and using it for "same-day" analysis of the cans. The basic approach would be to have an enclosed multipass cell, pump cans into this cell, acquire spectra for several minutes, then flush the cell and repeat on the next can. In this way 2 or 3 dozen cans could be analyzed within several hours of collection. Dr. Baker estimates the time requirements for a GC deployed in the field would be similar. Additional benefits could be realized by cleaning and reusing the cans. Dr. Baker estimates this would take another day for several dozen cans. The cleaning time depends on the pumps and gases available rather than the analysis technique. The major potential benefit of using the FTIR appears to be that results could be obtained for a larger variety of gas types as long as they survive brief can storage!

There are three key questions to answer regarding the desirability of such an activity: 1. Technical feasibility of providing the infrastructure needed for proper operation of the FTIR, 2. Probable accuracy of the FTIR can analysis, and 3. The desirability of using FTIR resources in this way as opposed to other activities. These key issues are addressed in turn below:

Technical feasibility is the easiest part to evaluate. The FTIR requires suitable power and liquid N_2 (LN_2) for the most sensitive detector. We found that LN_2 was widely available at welding supply vendors; in the US. In addition we purchased two storage dewars for use in the field: one was able to store LN_2 for up to 10 days, but was a bit large to bring on board a small plane. The other dewar stores LN_2 for three days and is small enough to transport with a full load of equipment and personnel on the King Air. Power can be supplied by using any 110 VAC, adapting 28VDC from plane, or by using any 12V battery or automobile cigarette lighter.

The accuracy of the FTIR analysis is described in the previous section and should already be adequate except for the cans where CO_2 is at very small enhancements. It may be possible to anticipate and reserve these cans for later GC analysis. Alternatively, the FTIR sensitivity can be improved by increasing the path-to-volume ratio of the multipass cell. Our current enclosed cell has a path of 97.5 meters and a volume of 16 liters for a ratio of ~ 6.1 ml^{-1}. A cell with a 25 meter path and 1 liter volume would make can analysis by FTIR about 4 times more sensitive and is available for about $2000 (the price of 5 cans).

Since the FTIR is used to measure many gases which are not traditionally measured from canister samples one might be concerned that this important ability may be underutilized by analyzing cans if these compounds do not survive brief can storage. Thus, we instituted a simple test to see how many of the gases we commonly measure by FTIR survived a brief storage in a stainless steel can. In this experiment we drew fresh

smoke into our multipass cell and measured the constituents. Next the smoke was transferred to three cans where it was stored for about 4 hours. Finally the smoke was re-transferred to the multipass cell where it was again analyzed by FTIR. This test has been performed once so far and preliminary results indicate losses for acetic acid of about 10%, formic acid of about 30%, and 2-hydroxyethanal of > 50%. Methanol, methane, and ethene seemed to store well along with CO and CO_2. More tests are needed to verify these effects and to investigate the fate of NH_3, HCN, NO, and other species in the cans. An 8-hour, smoke-storage test in our glass multipass cell indicated that significant loss of terpenes could occur within several hours as shown in Figure 5 of Part 3.

D. Participate in a conference on exposure of wildland firefighters to smoke and present results from current research at IFSL to the symposium participants (meeting tentatively scheduled in Missoula during April 1997).

Reinhardt et al measured an 8-h-average firefighter exposure to CO, formaldehyde and acrolien in the field. The CO was by a reliable technique, but the acrolien and formaldehyde were measured by a technique which may not perform well in smoke. The field study acrolien results suggested that exposure to this compound was of concern. In fact, this measurement of acrolien exposure is "driving" the current NWCG risk assessment.

We can build a laboratory fire large enough that any of the 89 gases defined as hazardous air pollutants (HAPS) by the EPA would be detectable in smoke by FTIR; if they were present at high enough *peak or average* levels to be a health concern (this includes formaldehyde or acrolien). The following HAPS *were* detected in real-time in smoke by FTIR: carbon monoxide, methane, ethane, ethene, ethyne, propene, formaldehyde, 2-hydroxyethanal, methanol, phenol, acetic acid, formic acid, nitric oxide, ammonia, hydrogen cyanide, sulfur dioxide, and carbonyl sulfide. However, in the 92 fires we studied, all these compounds were present at ratios to CO well below the level where the expected field exposure would exceed OSHA or NIOSH permissible peak or average exposures (based on Reinhardt et al field CO exposure data). This is especially true of acrolien where our FTIR results for acrolien/CO are at least an order of magnitude lower than Reinhardt et al. This suggests two valuable follow-up studies: 1. deployment of the FTIR in a fireline situation, and 2. intercomparison of the FTIR and the other acrolien measurement technique under controlled laboratory conditions.

The above results and relevant background were presented during a panel discussion and oral presentation, and in a poster at the NWCG national conference on Health Hazards of Smoke in April 1997 in Missoula. Copies of the abstract for the talk and the poster are attached.

Health Hazards of Smoke

USDA MTDC
April 8 - 10 1997

Panel Discussion: *What we need to know about emissions.*

Draft Summary of Remarks by Dr. Robert J. Yokelson

It is difficult to use conventional gas analysis techniques to directly measure reactive components of smoke or peak exposure levels. For this reason, Dr. Ward and the NWCG steering committee began supporting spectroscopic studies in 1989, which have continued through the present. These studies are capable of shedding light on the above topics because there is no sample collection step. Instead, light is shown through the smoke and characteristic absorption by the molecules therein is analyzed in real time. Two such measurements are shown from the same fire at two different times which illustrates the rapid change possible in smoke composition and the previously unknown, high relative importance of reactive gases. For some compounds (acetic acid, methanol, and formaldehyde) the spectroscopic measurements suggest exposure levels which are 2 - 1000 times what was previously measured, but not over the permissible limit. For other compounds (acrolien, acetone, and nitric acid) the spectroscopically determined exposure levels are comparatively much lower (at least a factor of 10 for acrolien). Peak concentrations for formaldehyde have been measured in large laboratory fires which are up to ~80 % of the IDLH. Whether this level of exposure is appropriate for a firefighter RME remains to be addressed by future field studies.

Health Hazards of Smoke

USDA MTDC
April 8 - 10 1997

POSTER: *Open-path Fourier transform infrared studies of smoke from large-scale laboratory biomass fires.*

Draft Summary of Content by Dr. Robert J. Yokelson

Open-path Fourier transform spectroscopy (OP-FTIR) is capable of measuring a wide variety of reactive and stable gases with high (seconds) time resolution. We have pioneered the use of this technique to determine the trace gases in smoke from biomass fires in a wide variety of fuel and fire types including: grasses, hardwoods, softwoods (coniferous), and organic soils. Large differences in emissions occur from different fire and fuel types, and during individual fires, demonstrating the value of continuous sampling. The observed fire behavior and chemistry is outlined and the gas phase products detected are classified by the type of process that dominates in producing them. From flaming combustion we measure carbon dioxide, nitric oxide, nitrogen dioxide, sulfur dioxide, and water vapor (from combustion and fuel moisture). From smoldering combustion we measure (carbon dioxide), carbon monoxide, methane, ammonia, and ethane. A significant fraction of the total emissions is unoxidized pyrolysis products; examples are methanol, phenol, formaldehyde, hydroxyacetaldehyde, acetic and formic acid, ethene (ethylene), ethyne (acetylene), propene, carbonyl sulfide, and hydrogen cyanide. Relatively few previous data existed for many of these reactive pyrolysis compounds and many are both quite abundant and classified by the Clean Air Act as air toxics. We have measured peak production levels and fire-integrated production relative to CO for these compounds, both of which can be used to estimate firefighter exposure levels in fresh smoke. Possible mechanisms for secondary gas phase production of other air toxics (downwind) are also presented.

2. Characterizing biomass fires and their emissions using an open-path Fourier transform infrared spectrometer

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Abstract

A series of 8 small scale open fires were studied in a controlled-environment combustion facility using a Fourier transform infrared (FTIR) spectrometer coupled to an open multi-pass cell. The fuels consisted of pure and mixed samples of grass, pine needles and fir litter simulating forest floor burns. Mid-infrared spectra of the smoke were recorded throughout each fire along with a simultaneous measurement of the fuel mass loss, stack gas temperature and total mass flow up the stack. The products detected are classified according to the dominant process generating them. From flaming combustion we measured carbon dioxide, nitric oxide and water vapor. From smoldering combustion we measured carbon dioxide, carbon monoxide, methane and ammonia. From fuel pyrolysis we measured methanol, formaldehyde, hydroxyacetaldehyde, acetic and formic acid, ethene, ethyne and propene. The FTIR results were also shown to be in excellent agreement with canister smoke samples taken during the fires and analyzed using GC/FID along with real-time CO and CO_2 results. In addition we have determined that 45-60% of the energy released by biomass combustion is absorbed in the convection column. This is an important factor in determining the final altitude of a smoke plume in a real fire.

Table 1. A summary of *in-situ,* spectroscopic, biomass fire emission measurements expressed as percentages of CO_2 and CO.

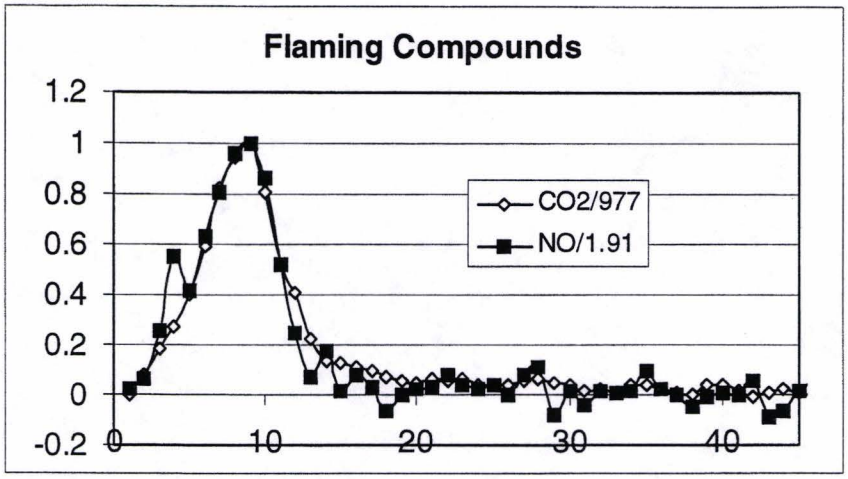
Study	Emissions as percent of CO_2		
	NO	SO_2	NO_2
Griffith et al., 1991	0.095	nm[1]	0.050
Yokelson et al., 1996	0.178	0.063	0.050
Australian Conf. Proc. 1996	0.128	nm	nm
This work	0.175	nm	nm

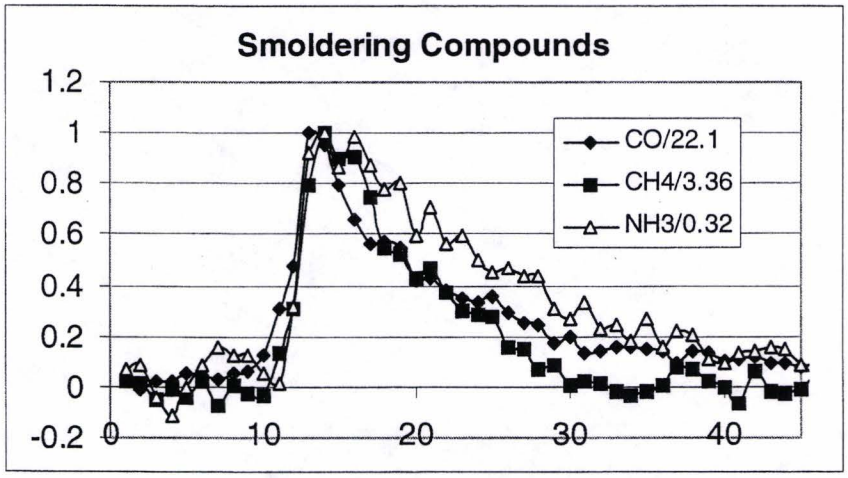
	Emissions as percent of CO													
	Hydrocarbons					Aldehydes		Acids		Alcohols		Nitrogen		Sulfur
	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	HCHO	Glycol-	Formic	Acetic	CH_3OH	C_6H_6O	NH_3	HCN	OCS
Griffith et al., 1991	7.61	nm	nm	nm	nm	1.27	nm	nm	nm	nm	nm	3.24	0.12	nm
Yokelson et al., 1996	10.86	1.42	1.71	0.98	nm	1.60	nm	0.73	2.32	1.61	nm	1.91	0.44	nm
Yokelson et al., 1997	6.55	0.45	0.98	0.17	0.65	2.33	1.08	1.09	2.20	1.98	0.84	2.66	0.65	0.04
Australian Conf. Proc. 1996	6.43	nm	1.49	nm	nm	1.55	nm	0.58	1.12	1.21	nm	1.42	nm	nm
This work	7.83	nm	2.13	0.25	1.73	nm	0.37	0.77	1.50	0.92	nm	1.31	nm	nm
Average published	7.86	0.94	1.39	0.57	0.65	1.69	1.08	0.80	1.88	1.60	0.84	2.31	0.40	0.04

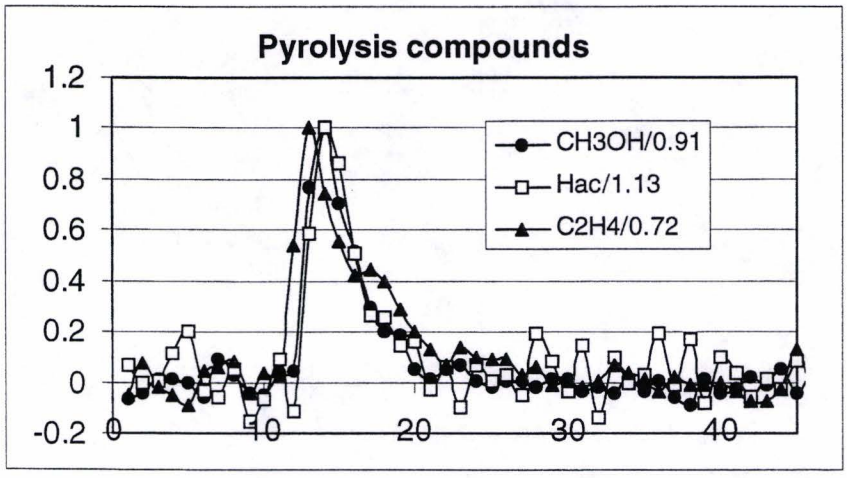
[1]nm, not measured.

Table 2. Emission results for series of fires expressed as 100 x moles compound/moles of carbon detected

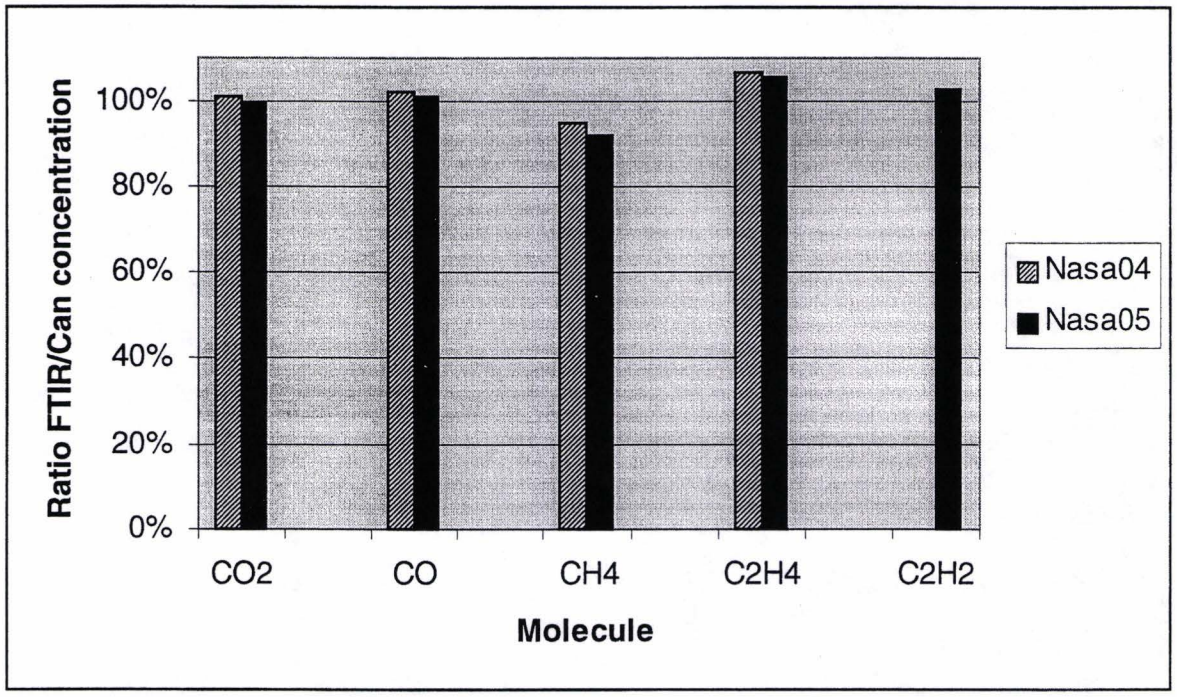
Fire/Fuel	MCE	CO2	CO	CH4	NO	CH2O	C2H4	C2H2	NH3	CH3OH	CH3COOH	HCOOH	C2H4O2
	%												
Ponderosa pine needles (PPN)	96.7	95.96	3.38	0.365	0.164	bdl	0.050	0.005	0.063	0.047	0.057	bdl	bdl
Grass	94.5	93.78	5.07	0.521	0.229	0.038	0.074	0.007	0.097	0.064	0.116	bdl	0.094
Douglas Fir litter on PPN starter	95.3	94.55	4.64	0.394	0.079	bdl	0.075	0.020	0.040	0.060	0.077	0.014	bdl
PPN backing fire - 40% slope	97.7	97.34	2.28	0.142	0.126	bdl	0.101	0.008	0.028	bdl	bdl	bdl	bdl
Grass backing fire - 40% slope	95.9	95.74	4.03	0.232	0.179	bdl	0.044	bdl	0.056	0.016	0.017	bdl	bdl
Pine litter over PPN backing fire - 40% slope	97.2	97.13	2.64	0.154	0.143	bdl	0.024	bdl	0.020	0.009	bdl	bdl	bdl







Example of time evolution for compounds emitted from a fire in a fuel of moist pine needles separated by flaming, smoldering and pyrolysis/distillation combustion process.



Intercomparison between smoke samples taken in stainless steel canisters and analyzed using GC/FID and the continuous measurements recorded using the OP-FTIR for two fires.

3. Monoterpenes: Infrared Cross-sections and Concentration in Smoke.

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Abstract. Monoterpenes are 10 carbon compounds which are stored in and emitted from plant tissues. These compounds have an important influence on global tropospheric chemistry through their fast reactions with OH, O_3, and NO_3. The mid-infrared (IR) absorption cross-section was measured for five of the more common monoterpenes α-pinene, β-pinene, Δ^3-carene, limonene, and myrcene. The spectra are found to be independent of resolution from 0.01 to 2.0 cm^{-1} which is the usual range of resolution used in FTIR measurements. The cross-sections are sufficiently strong to give peak absorbances (base 10) with a 100 m path near the commonly reported IR detection limit of 0.0001 with 1.5 x 10^{10} molecules cm^3. This concentration is approximately 0.5 ppb at mean sea level and lower than the peak mixing ratios measured in the field for these compounds of ~ 5.0 ppb. This indicates that long-path Fourier transform infrared spectroscopy (FTIR) might provide a useful optical remote sensing measurement of these molecules at higher ambient levels. Accurate cross-sections for these molecules will also be of use in IR-based laboratory studies of their chemistry. Our open-path FTIR smoke spectra suggest that these compounds are important emissions from biomass fires and may account for over 1% of the fuel carbon burned. At these concentrations they would be expected to have a significant influence on the local-regional O_3 formation chemistry in smoke plumes from biomass fires. A smoke storage experiment was conducted in the dark in a glass multipass cell. The results indicated that these compounds may be lost (in smoke) over ~ 8 hours in some containers used for storage of atmospheric samples.

Methods and Materials

Reference Spectra

Reference spectra for monoterpenes were acquired at the NOAA Aeronomy Laboratory. IR Energy from a graphite lamp (4 Volts ~ 22 amps) was directed through a 2.5 micron long-pass filter and then a 15 cm absorption cell installed in the sample compartment of a Bomem (model Dxx) FTIR; then through the interferometer, and onto an InSb detector. Pressure in the absorption cell was monitored by a xxx transducer for reading cell pressure values near vacuum and by a xxxx transducer for reading cell pressure when filled with sample (typically 0.3 - 3 torr). The cell was also connected by 4 mm ((o.d.) teflon tubing to traps containing liquid terpene samples used directly as obtained from Aldrich. The sample purity claimed by the manufacturer was 99, 98, and 90 % for β-pinene, α-pinene, and Δ^3-carene respectively. The cell was also connected to UHP N_2, and a vacuum pump. The sample compartment was assumed to be at room temperature. Initially, the spectrum of α-pinene was recorded at both 0.01 and 2.0 cm^{-1} resolution (which more than spans the normal range of resolution used in relevant types of studies). The spectra recorded at these two resolutions were identical indicating that the cross-sections are independent of resolution over this range. We used a resolution of 0.12 cm^{-1} for all subsequent spectra to facilitate their use in analyzing a number of our smoke spectra acquired at the same resolution. For each monoterpene, a background spectrum was acquired (after pumping out and flushing the cell) by coadding 50 scans (acquired at 0.12 cm^{-1} resolution) over the spectral range of 2750 to 3100 cm^{-1}. Subsequently, the cell was filled to a variety of pressures of the monoterpene and sample

spectra were acquired at each of those pressures using operating parameters identical to those for the background spectra. For limonene and myrcene, which were expected to be less common only one sample pressure was used. A pressure giving a large sample absorbance was chosen to minimize error.

Smoke spectra

Smoke spectra were acquired at the Intermountain Fire Sciences Laboratory as described in detail elsewhere [3 ref]. The fuels were burned on a ~ 1 x 2 m continuously-weighed fuel bed, and the smoke captured by a 1.6 m diameter stack with a 3.6 m inverted funnel opening just above the fuel bed. A sampling platform surrounds the stack 15 meters above the fuel bed. Spectra were acquired by two methods. In method 1 [Yokelson et al., 1996a, b], an IR source was collimated and transmitted twice across the stack through the smoke for a total smoke absorption path of 3 m, then focused and re-collimated into an EOCOM spectrometer with a Ge/KBr beamsplitter, and an InSb/MCT detector. This instrument was operated at a spectral resolution of 0.12 cm-1 and a temporal resolution of 0.5 to 4 minutes. In method 2, the IR radiation from within the FTIR (MIDAC model 2500) is directed through a 1.6 m basepath open White cell (I. R. Analysis), and then refocused on an external "wideband" MCT detector (Graseby FTIR M-16). The White cell allowed path lengths up to 76.5 m in the experiments reported here. The MIDAC spectrometer was operated with a time resolution of 3 seconds and spectral resolution of 0.5 cm^{-1} [*Yokelson et al.*, 1997a, b].

Results and Discussion

Reference Spectrum Data Analysis

The monoterpene spectra are independent of resolution from 0.01 to 2.0 cm^{-1} consistent with the finding of Hanst and Hanst [199x] that the cross-sections of α- and β-pinene are resolution independent between 0.125 and 0.5 cm^{-1}. The resolution independence indicates that the values for the cross-section we report here are appropriate for most of the experimental conditions for environmental measurements reported in the literature.

The cross-section data were subsequently reduced as follows. For α-pinene, β-pinene, and Δ^3-carene the frequency at which the maximum absorbance was observed (or, in the case of α-pinene, the frequency of a distinctive feature near the maximum value) was adopted as a reference frequency for plotting absorbance against pressure. Linear regression was used to fit a line to these plots and high correlation ($r^2 \sim 0.99$) was observed in all cases (See Figure 1.) The peak cross-section values for α-pinene, β-pinene, and Δ^3-carene are reported in Table 1 and they are derived from the slopes of these plots. The quoted uncertainties in the cross-section are derived from the standard error in the slopes and are for 95% confidence intervals. In all cases the uncertainty for this confidence interval is less than 1% of the peak cross-section value. We are aware of two other reported measurements suitable for comparison [Hanst library]. Those values are also included in Table 1. For α-pinene our cross-section value at 2924.8 cm^{-1} is 2.4 % lower than the value in the Hanst Library for which a nominal accuracy of 5 % is claimed. However, our value for the β-pinene cross-section at 2921.5 cm^{-1} is 13 % lower than the

value in the Hanst library. Without knowing more about how their spectra were obtained we cannot speculate on the cause for this discrepancy.

For limonene and myrcene the peak cross-sections are based on the absorbance at one pressure only. The major potential sources of error in a single point measurement would likely be offsets arising from inaccurate pressure measurement or absorbance due to the sample sticking to the cell walls. These effects would cause a systematic deviation of the intercept from zero in our multipoint plots. In fact the intercepts for these plots are both positive and negative and average to -0.6%. The accuracy of these one-point cross-section determinations can be estimated by analysis of the multipoint measurements as follows. For the α-pinene, β-pinene, and Δ^3-carene data set we compare the slopes obtained using one point only to that obtained from the multipoint determination. The average of the single point slopes is 98% of the multipoint value with a standard deviation of 8.8%. Thus, we conclude that a rigorous estimate of the accuracy of the single-point cross-section determinations is about 10 % (1σ). A reference spectrum for each compound is plotted in Figure 2 in cross-section units referenced to absorbance base 10.

Figure Captions

Figure 1. Sample absorbance is highly correlated with sample pressure for the indicated monoterpenes. The linear fit is used to derive cross-section values which should discriminate against errors caused by sample handling difficulties.

Figure 2. The "C-H stretch" IR spectrum is shown in the indicated cross-section units for (a) a-pinene and b-pinene and (b) D3-carene, limonene, and myrcene. These are the dominant monoterpenes in the chromatogram published by Westberg [1981].

Figure 3. The "C-H stretch" absorbance spectrum for a mixture of monoterpenes (described in text) is coplotted with smoke spectra. The smoke spectra show sharp features due to water, methane, and formaldehyde. The smoke spectrum is from burning pine needles in (a) and burning sagebrush in (b).

Figure 4. Multiple CLS fit examples.

Figure 5. Smoke storage results.

Table 1. Infrared cross-section data for 5 monoterpenes.

Molecule	Peak Frequency	σ_{10} cm^2 mol^{-1}	r^2 slope
α-pinene[1]	2924.8	6.58×10^{-19}	0.9982
β-pinene[2]	2921.5	4.43×10^{-19}	0.9922
Δ^3-carene[3]	2881.9	2.06×10^{-19}	0.9898
	2876.2	"	
limonene	2930.8	2.75×10^{-19}	na
myrcene	2938.8	2.08×10^{-19}	na

[1]Value of cross-section in Hanst 6.74×10^{-19}.
[2]Frequency given is for sharp peak near maximum. Hanst reports 5.12×10^{-19} for σ at this frequency.
[3]Δ^3-carene has two equally intense peaks.

Fire-Integrated Data From February Stack Fires																		
These are all high-CE, full-scale fires (with flaming and smoldering) in fine, dry fuels																		
		Fire-average concentrations															w/terps	
Filename		**CO_2**	**CO**	**CH_4**	**CH_2O**	**CH_3OH**	**Formic**	**Acetic**	**C_2H_4**	**NH_3**	**NO**	**b-pin**	**caren**	**limon**	**MCE**	**CTOT**	**CTOT**	**terptot**
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		ppm	ppm	**CO**
011wfa	P pine + DAP	286	20.37	2.100	0.183	0.351	bld	0.232	0.248	0.299	0.322	0.309	0.251	0.913	0.934	310.0	324.7	0.72
014wfa	Douglas Fir (vertical)	255	16.08	0.726	0.306	0.052	0.088	0.074	0.250	0.278	0.350	0.131	0.086	0.18	0.941	272.9	276.9	0.25
272wfa	Poplar shavings	330	16.06	1.244	0.435	0.433	0.159	0.251	0.400	0.231	0.304	0.201	0.231	0.343	0.954	349.6	357.4	0.48
281wfa	P pine	537	29.58	1.181	0.306	0.130	0.123	bld	0.443	0.350	0.978	0.154	0.119	0.177	0.948	569.2	573.7	0.15
282wfa	P pine + wind	291	18.33	0.670	0.194	0.115	bld	bld	0.240	0.216	0.253	0.13	0.075	0.231	0.941	310.8	315.1	0.24
292wfa	Sagebrush	699	44.95	3.561	0.880	0.735	bld	0.616	0.499	0.695	1.114	0.315	0.363	0.14	0.940	751.4	759.5	0.18
AVG ALL		**399.7**	**24.23**	**1.580**	**0.384**	**0.303**	**0.123**	**0.293**	**0.347**	**0.345**	**0.554**	**0.207**	**0.188**	**0.331**	**0.943**	**427.3**	**434.6**	**0.338**

SOME PRELIMINARY TERPENE RESULTS FOR SMOLDERING COMBUSTION

	Excess Concentrations from absorption spectra																			Est.				Est.	
	Oxides			*Hydrocarbons*				*Aldehydes*		*Organic Acids*		*Alcohols*		*Terpenes*				*molar*	*carbon*	*Total C*	*Nitrogen Compounds*			*Total N*	*Sulfur*
Fuel Type	**CO_2**	**CO**	***MCE***	**CH_4**	**C_2H_4**	**C_2H_2**	**C_3H_6**	**HCHO**	**HAAH**	**Formic**	**Acetic**	**CH_3OH**	**C_6H_6O**	**a-pin**	**b-pin**	**car**	**lim**	**terpenes**	**terpenes**	**C_{TOT}**	**NH_3**	**HCN**	NH3/HCN	**N_{TOT}**	**OCS**
	ppm	ppm	CO_2/CO_2+CO	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	methane	methane	ppm	ppm	ppm		ppm	ppm
bannana leaves fpg	125.74	23.89	***0.840***	1.288	0.541	0.050	0.741	0.745	0.281	0.047	0.345	0.747	0.089	0.084	0.323	0.202	1.303	1.485	14.8	177.04	3.843	0.257	14.953	4.100	0.016
bannana leaves fpg	122.59	23.81	***0.837***	1.265	0.543	0.050	0.768	0.741	0.289	0.055	0.337	0.746	0.086	0.088	0.319	0.210	1.301	1.516	15.2	173.93	3.729	0.275	13.560	4.004	0.017
Mont.bunch grass fpg	136.41	16.22	***0.894***	0.577	0.423	0.128	0.072	0.753	0.216	0.275	0.334	0.202	0.069	bld	0.130	0.260	0.548	1.624	16.2	166.77	0.057	0.128	0.445	0.185	0.008
Mont.bunch grass fpg	119.16	14.25	***0.893***	0.39	0.147	0.050	0.056	0.539	0.154	0.244	0.414	0.253	0.243	bld	0.112	0.213	0.511	2.143	21.4	146.48	0.24	0.125	1.920	0.365	0.004
Mont.bunch grass fpg	1263.70	103.25	***0.924***	3.379	2.304	0.585	0.405	4.131	0.947	1.395	2.364	1.115	0.790	bld	0.731	1.884	2.826	1.610	16.1	1451.24	1.586	1.453	1.092	3.039	0.053
Mont.bunch grass fpg	484.66	88.14	***0.846***	4.753	1.590	0.285	0.764	4.643	1.088	1.355	2.874	1.872	1.198	bld	1.020	1.966	3.511	1.367	13.7	672.50	2.294	0.886	2.589	3.180	0.055
Mont.bunch grass pg	91.36	27.96	***0.766***	1.188	0.346	0.028	0.227	1.509	0.345	0.575	1.236	0.776	0.425	bld	0.236	0.728	1.355	1.952	19.5	154.04	1.09	0.326	3.344	1.416	0.022
Mont.bunch grass pg	100.68	30.84	***0.766***	1.415	0.340	0.033	0.249	1.342	0.351	0.613	1.245	0.836	0.607	bld	0.181	0.796	1.467	1.727	17.3	168.84	1.139	0.329	3.462	1.468	0.018
Mont.bunch grass pg	88.47	27.79	***0.761***	1.307	0.313	0.021	0.215	1.098	0.387	0.562	1.093	0.683	0.057	bld	0.140	0.694	1.304	1.637	16.4	146.28	1.038	0.343	3.026	1.381	0.020
Mont.bunch grass pg	49.77	19.11	***0.723***	0.846	0.229	0.019	0.210	0.855	0.307	0.698	1.552	0.802	0.487	bld	0.069	0.623	1.102	2.121	21.2	98.04	0.416	0.24	1.733	0.656	0.010
Mont.bunch grass pg	155.94	20.14	***0.886***	1.048	0.189	0.023	0.097	0.641	0.197	0.381	0.655	0.475	0.402	bld	0.265	0.110	1.014	1.325	13.3	197.57	0.495	0.219	2.260	0.714	0.005
Wire grass fgp	349.60	39.95	***0.897***	1.423	0.194	0.027	0.191	0.232	0.114	0.051	0.205	0.177	0.159	0.011	0.093	0.132	0.293	0.371	3.7	399.50	0.887	0.166	5.343	1.053	0.020
Wire grass fgp	80.46	14.01	***0.852***	1.055	0.080	0.020	0.078	0.059	0.029	0.017	0.020	0.168	0.000	bld	0.071	0.059	0.102	0.220	2.2	98.68	0.581	0.053	10.962	0.634	0.004
Alaska peat pg	33.66	9.62	***0.778***	0.275	0.044	0.004	0.056	0.125	0.025	0.080	0.159	0.077	0.022	0.006	0.017	0.075	0.215	1.144	11.4	47.83	0.106	0.079	1.342	0.185	0.002
Alaska peat pg	32.66	8.9	***0.786***	0.264	0.040	0.004	0.075	0.111	0.025	0.080	0.186	0.077	0.011	0.009	0.010	0.070	0.231	1.212	12.1	46.20	0.155	0.1	1.550	0.255	0.003
Pine-oak (SE) duff fpg	195.09	15.29	***0.927***	0.353	0.212	0.068	0.074	0.249	0.022	0.092	0.119	0.141	0.035	bld	0.155	0.118	0.417	1.956	19.6	219.41	0.063	0.012	5.250	0.075	0.006
Pine-oak (SE) duff fpg	140.69	15.81	***0.899***	0.509	0.158	0.038	0.096	0.269	0.054	0.141	0.276	0.310	0.082	bld	0.166	0.206	0.887	2.474	24.7	172.18	0.078	0.025	3.120	0.103	0.005
Pine-oak (SE) duff fpg	254.21	40.33	***0.863***	1.202	0.634	0.191	0.215	0.848	0.125	0.326	0.482	0.590	0.035	bld	0.536	0.494	1.641	2.222	22.2	328.15	0.136	0.186	0.731	0.322	0.023
Pine-oak (SE) duff fpg	480.57	37.76	***0.927***	1.233	0.531	0.132	0.137	0.664	0.085	0.259	0.470	0.554	0.112	bld	0.421	0.500	1.308	1.808	18.1	547.10	0.166	0.232	0.716	0.398	0.017
Pine-oak (SE) duff fpg	248.56	31.02	***0.889***	1.227	0.331	0.103	0.069	0.569	0.061	0.212	0.343	0.450	0.202	bld	0.337	0.322	0.891	1.263	12.6	300.65	0.157	0.01	15.700	0.167	0.011
Pine-oak (SE) duff fpg	89.50	25.15	***0.781***	1.265	0.180	0.025	0.148	0.499	0.051	0.204	0.412	0.580	0.060	bld	0.188	0.298	0.701	0.938	9.4	131.35	0.071	0.132	0.538	0.203	0.013
Pine-oak (SE) duff pg	28.86	19.21	***0.600***	1.555	0.108	0.000	0.123	0.339	0.055	0.197	0.414	0.635	0.117	0.016	0.039	0.289	0.700	0.672	6.7	63.62	0.024	0.142	0.169	0.166	0.010
Pine-oak (SE) duff pg	61.85	30.13	***0.672***	1.479	0.146	0.005	0.125	0.428	0.050	0.164	0.334	0.519	0.174	0.013	0.182	0.326	1.153	1.132	11.3	113.98	0.083	0.159	0.522	0.242	0.017
Rotten P pine fpg	29.93	8.11	***0.787***	0.23	0.020	0.007	0.034	0.326	0.022	0.072	0.069	0.261	0.034	bld	0.052	0.054	0.066	0.748	7.5	41.20	0.035	0.012	2.917	0.047	0.000
Rotten P pine fpg	478.69	76.14	***0.863***	5.691	1.777	0.473	0.365	3.157	0.224	0.644	0.687	1.746	0.479	bld	1.024	0.837	2.268	0.726	7.3	617.80	0.09	0.115	0.783	0.205	0.037
Rotten P pine fpg	525.52	101.72	***0.838***	9.082	1.703	0.342	0.476	2.919	0.143	0.482	0.650	1.844	0.690	bld	1.257	1.090	2.638	0.549	5.5	702.90	0.347	0.191	1.817	0.538	0.048
Rotten P pine fpg	318.36	79.89	***0.799***	4.234	0.364	0.055	0.196	1.662	0.082	0.242	0.307	0.987	0.177	bld	0.478	0.412	0.822	0.404	4.0	425.95	0.695	0.146	4.760	0.841	0.036
Rotten P pine pg	184.85	59.14	***0.758***	4.067	0.287	0.022	0.190	1.717	0.067	0.291	0.448	1.370	0.306	bld	0.584	0.526	1.213	0.571	5.7	278.90	0.227	0.152	1.493	0.379	0.030
Rotten P pine pg	237.32	92.82	***0.719***	8.953	0.535	0.029	0.269	2.839	0.159	0.445	0.635	2.270	0.671	bld	0.967	1.052	1.392	0.381	3.8	386.59	0.196	0.249	0.787	0.445	0.043
Rotten P pine pg	260.47	88.04	***0.747***	9.237	0.438	0.028	0.207	2.344	0.167	0.542	0.435	1.740	0.745	bld	0.635	0.844	0.554	0.220	2.2	390.12	0.256	0.148	1.730	0.404	0.039
Palmetto-gallberry pg	118.66	29.61	***0.800***	2.36	0.193	0.013	0.173	0.111	0.013	0.013	0.108	0.130	0.000	bld	0.154	0.118	0.103	0.159	1.6	155.97	0.813	0.155	5.245	0.968	0.014
Sumter duff fgp	100.50	36.9	***0.731***	1.85	0.255	0.062	0.179	0.982	0.219	0.352	0.743	1.134	0.293	0.023	0.234	0.548	1.516	1.254	12.5	169.97	0.119	0.175	0.680	0.294	0.017
Sumter duff gp	32.28	18.95	***0.630***	1.559	0.141	0.010	0.141	0.596	0.142	0.255	0.759	0.911	0.160	0.035	0.064	0.482	1.166	1.120	11.2	75.62	0.061	0.116	0.526	0.177	0.007
Feather middle gp	52.03	14.57	***0.781***	0.539	0.099	0.005	0.139	0.236	0.036	0.109	0.376	0.261	0.046	0.071	0.058	0.153	0.813	2.030	20.3	80.58	0.16	0.164	0.976	0.324	0.006
Feather middle gp	103.56	27.87	***0.788***	1.543	0.205	0.013	0.200	0.282	0.018	0.081	0.347	0.291	0.043	0.111	0.160	0.127	1.059	0.944	9.4	150.52	0.762	0.284	2.683	1.046	0.015
Feather middle gp	90.09	24.12	***0.789***	1.383	0.172	0.008	0.188	0.187	0.020	0.065	0.264	0.207	0.000	0.125	0.023	0.134	0.893	0.849	8.5	129.51	0.536	0.215	2.493	0.751	0.012
Feather middle gp	81.63	23.79	***0.774***	1.513	0.141	0.006	0.154	0.150	0.012	0.064	0.243	0.183	0.000	0.160	-0.020	0.136	1.030	0.863	8.6	121.92	0.451	0.254	1.776	0.705	0.011
Mont.bunch grass fpg	412.97	33.4	***0.925***	1.019	0.696	0.205	0.238	1.240	0.235	0.357	0.732	0.337	0.296	bld	0.199	0.390	0.667	1.232	12.3	468.38	0.523	0.256	2.043	0.779	0.013
Mont.bunch grass fpg	130.61	27.64	***0.825***	1.212	0.396	0.095	0.185	1.108	0.271	0.304	0.860	0.631	0.243	bld	0.261	0.434	0.745	1.188	11.9	181.38	0.407	0.204	1.995	0.611	0.014
Mont.bunch grass fpg	58.29	8.22	***0.876***	0.29	0.293	0.149	0.069	0.287	0.015	0.097	0.000	0.039	0.000	0.008	0.028	0.036	0.140	0.731	7.3	70.56	0.021	0.097	0.216	0.118	0.000
Mont.bunch grass fpg	378.71	56.93	***0.869***	2.681	1.843	0.604	0.390	2.844	0.720	1.015	1.216	0.825	0.393	0.008	0.595	1.041	2.639	1.597	16.0	498.82	0.4	0.664	0.602	1.064	0.032
Palmetto-gallberry pg	160.09	34.18	***0.824***	2.241	0.202	0.015	0.208	0.408	0.077	0.000	2.402	1.171	0.979	bld	0.338	0.468	1.108	0.854	8.5	229.36	0.954	0.218	4.376	1.172	0.020
	202.11	36.30	**0.813**	2.119	0.461	0.096	0.219	1.066	0.188	0.320	0.646	0.693	0.262	0.051	0.306	0.463	1.086	1.20	12.0	266.61	0.607	0.231	3.148	0.838	0.018
compound id's repeated	**CO_2**	**CO**	***MCE***	**CH_4**	**C_2H_4**	**C_2H_2**	**C_3H_6**	**HCHO**	**HAAH**	**Formic**	**Acetic**	**CH_3OH**	**C_6H_6O**	**a-pin**	**b-pin**	**car**	**lim**	**terpenes**	**terpenes**	**C_{TOT}**	**NH_3**	**HCN**	NH3/HCN	**N_{TOT}**	**OCS**
																		methane	methane						

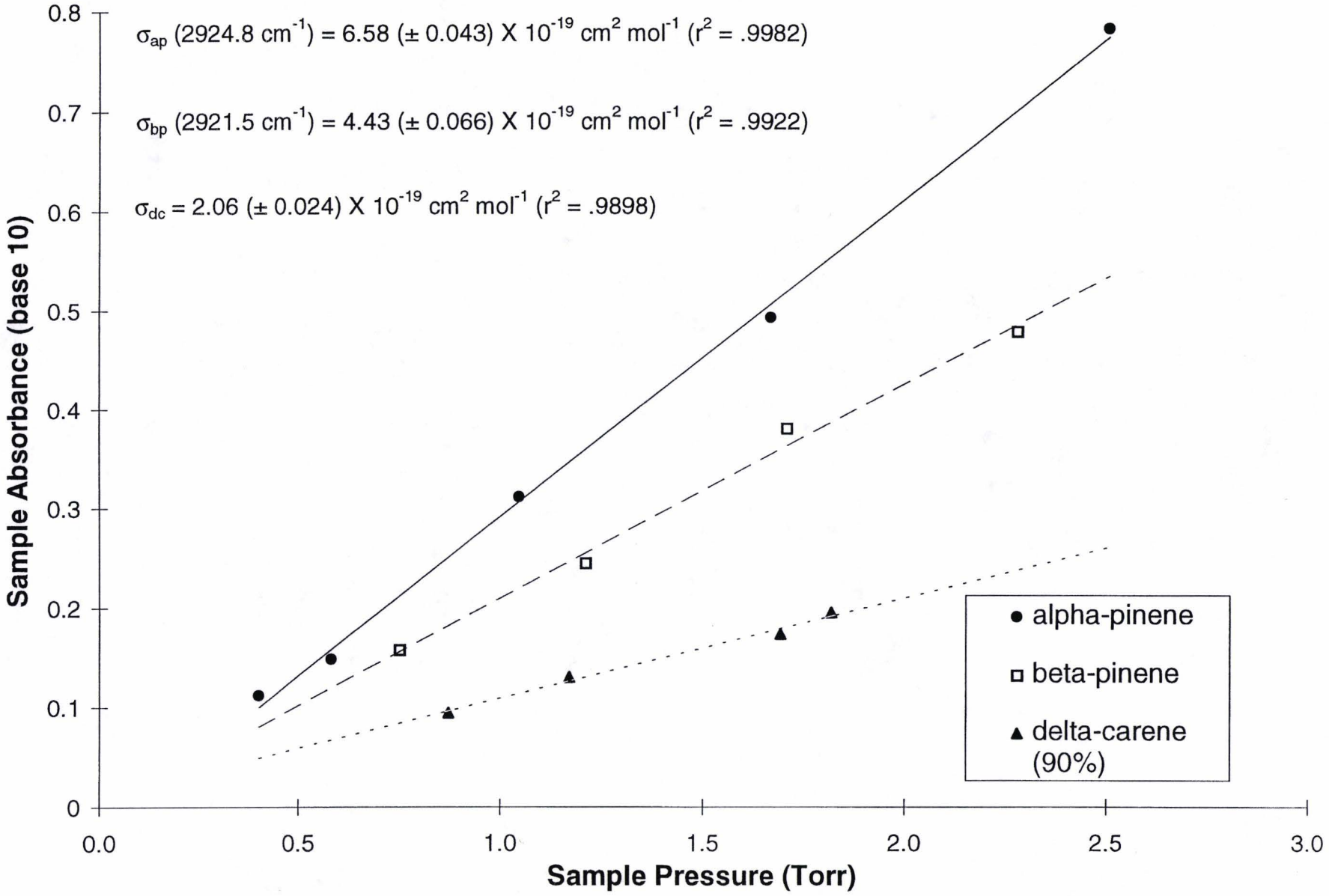
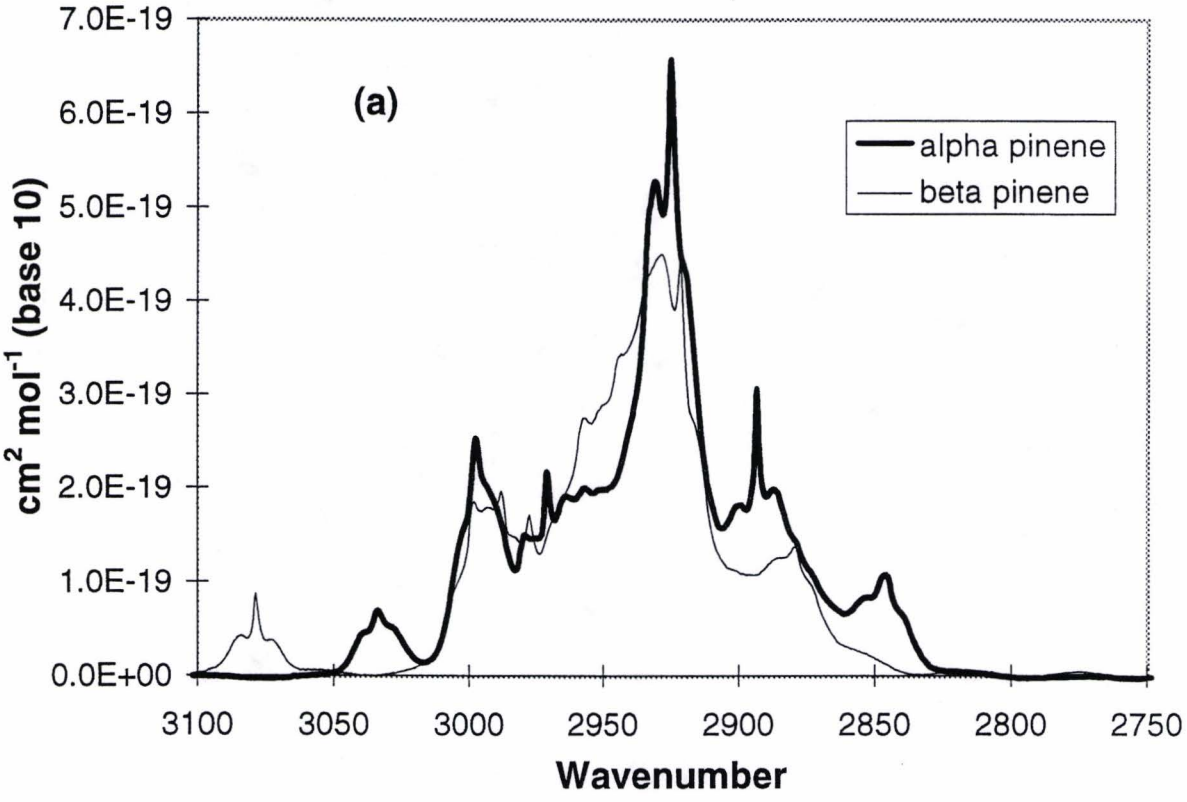

σ_{ap} (2924.8 cm^{-1}) = 6.58 (± 0.043) X 10^{-19} cm^2 mol^{-1} (r^2 = .9982)
σ_{bp} (2921.5 cm^{-1}) = 4.43 (± 0.066) X 10^{-19} cm^2 mol^{-1} (r^2 = .9922)
σ_{dc} = 2.06 (± 0.024) X 10^{-19} cm^2 mol^{-1} (r^2 = .9898)
Sample Absorbance (base 10)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Sample Pressure (Torr)
alpha-pinene
beta-pinene
delta-carene (90%)

Figure 1


(a)
alpha pinene
beta pinene
7.0E-19
6.0E-19
5.0E-19
4.0E-19
3.0E-19
2.0E-19
1.0E-19
0.0E+00
cm2 mol-1 (base 10)
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumber

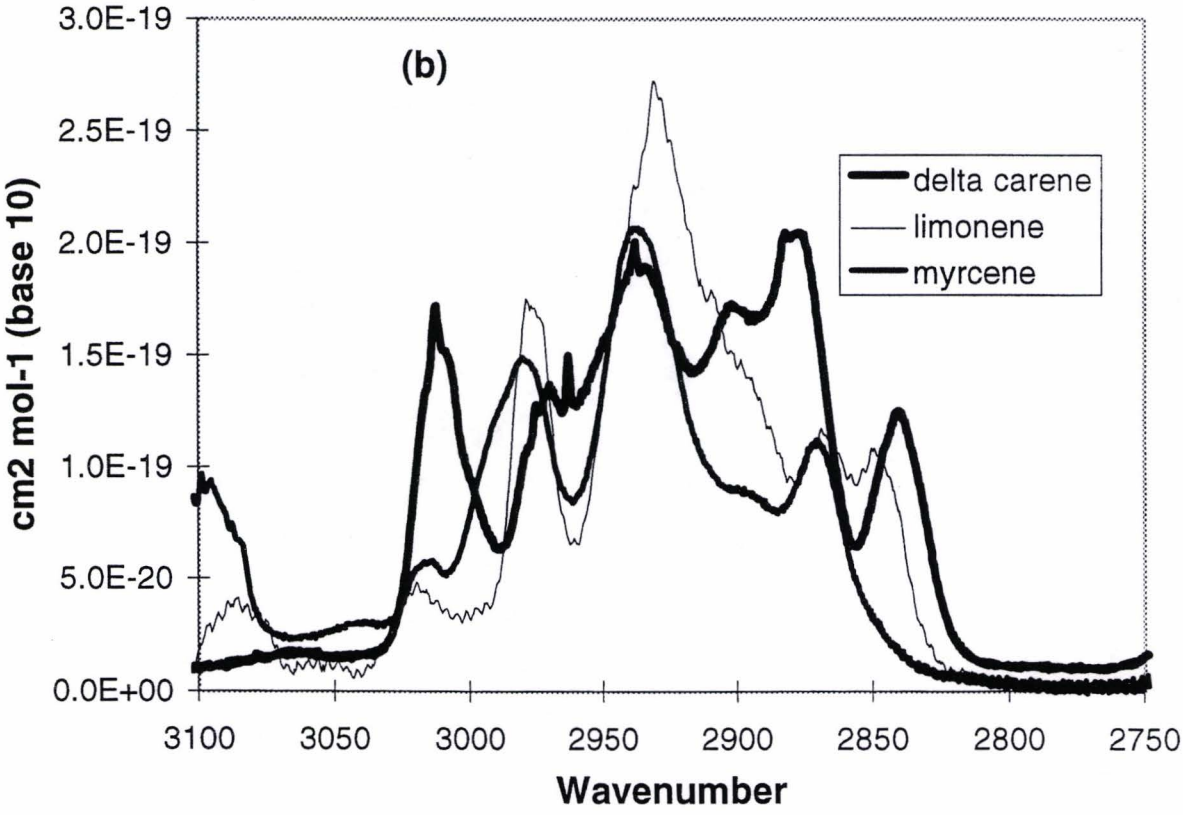
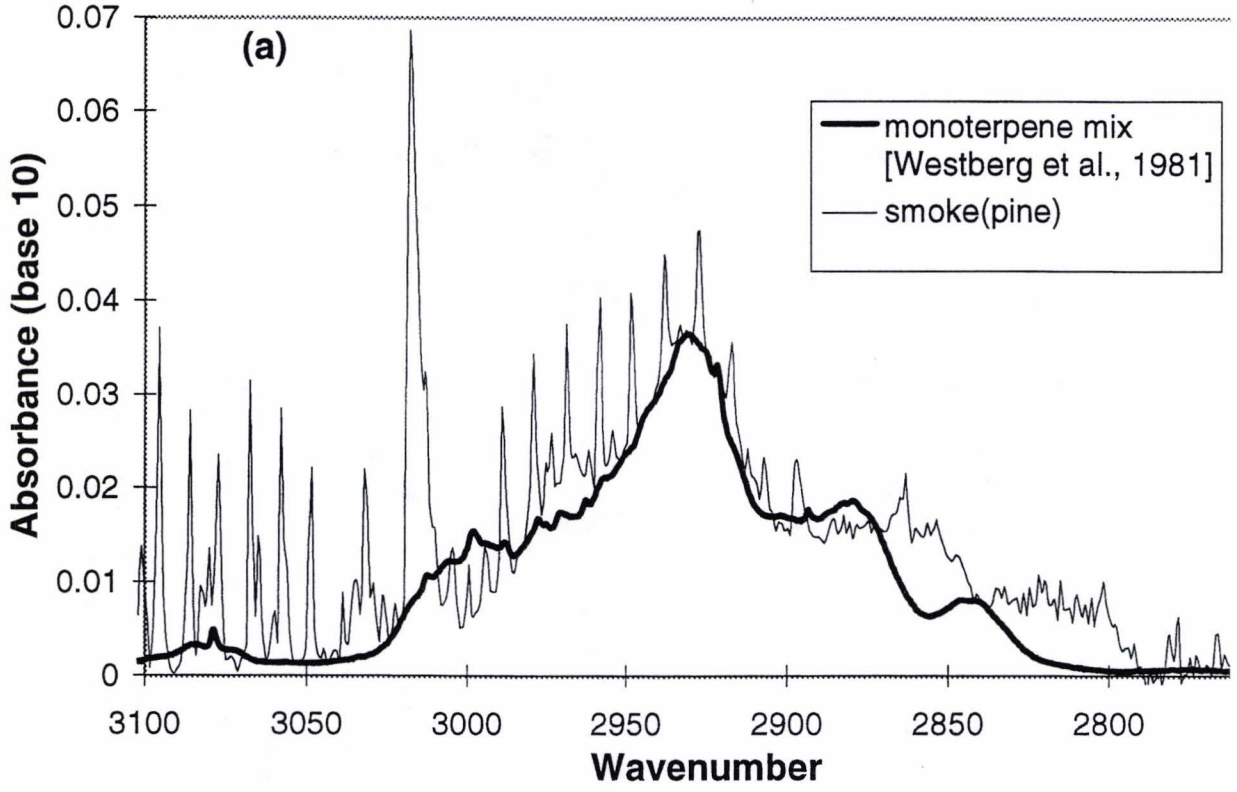

(b)
delta carene
limonene
myrcene
3.0E-19
2.5E-19
2.0E-19
1.5E-19
1.0E-19
5.0E-20
0.0E+00
cm2 mol-1 (base 10)
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumber

Figure 2


(a)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Absorbance (base 10)
monoterpene mix
[Westberg et al., 1981]
smoke(pine)
3100
3050
3000
2950
2900
2850
2800
Wavenumber

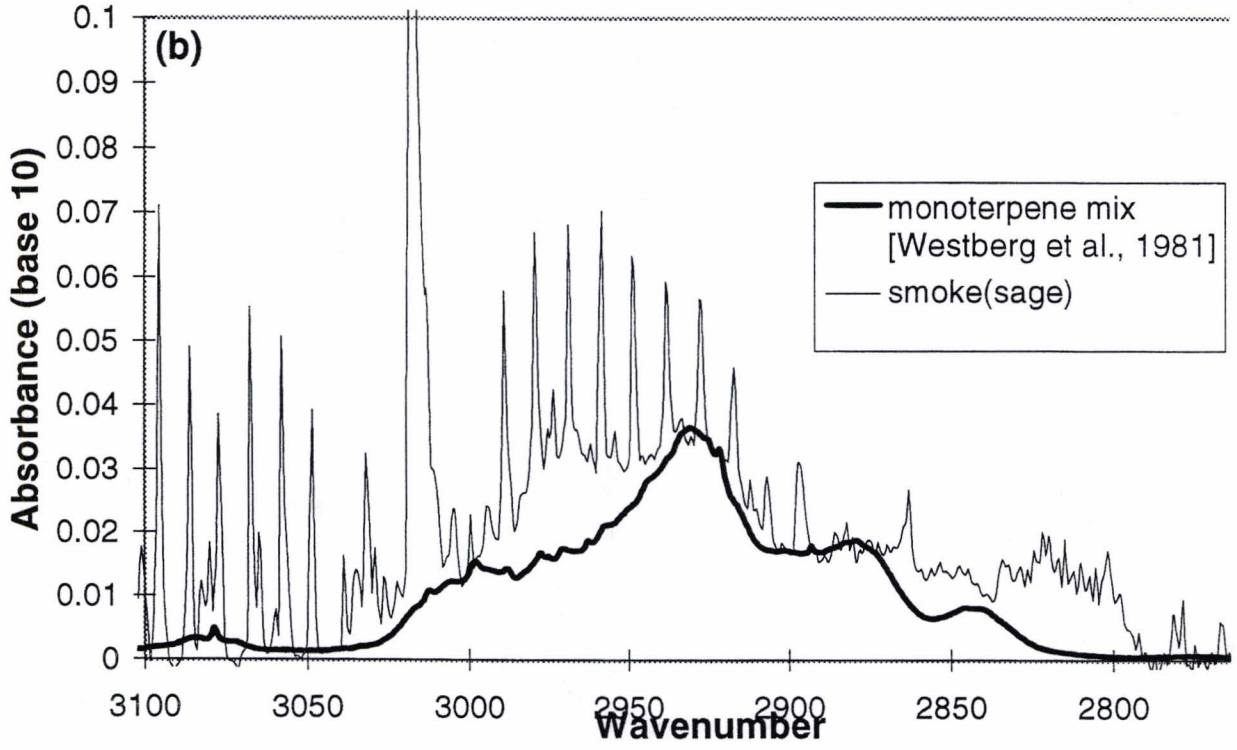
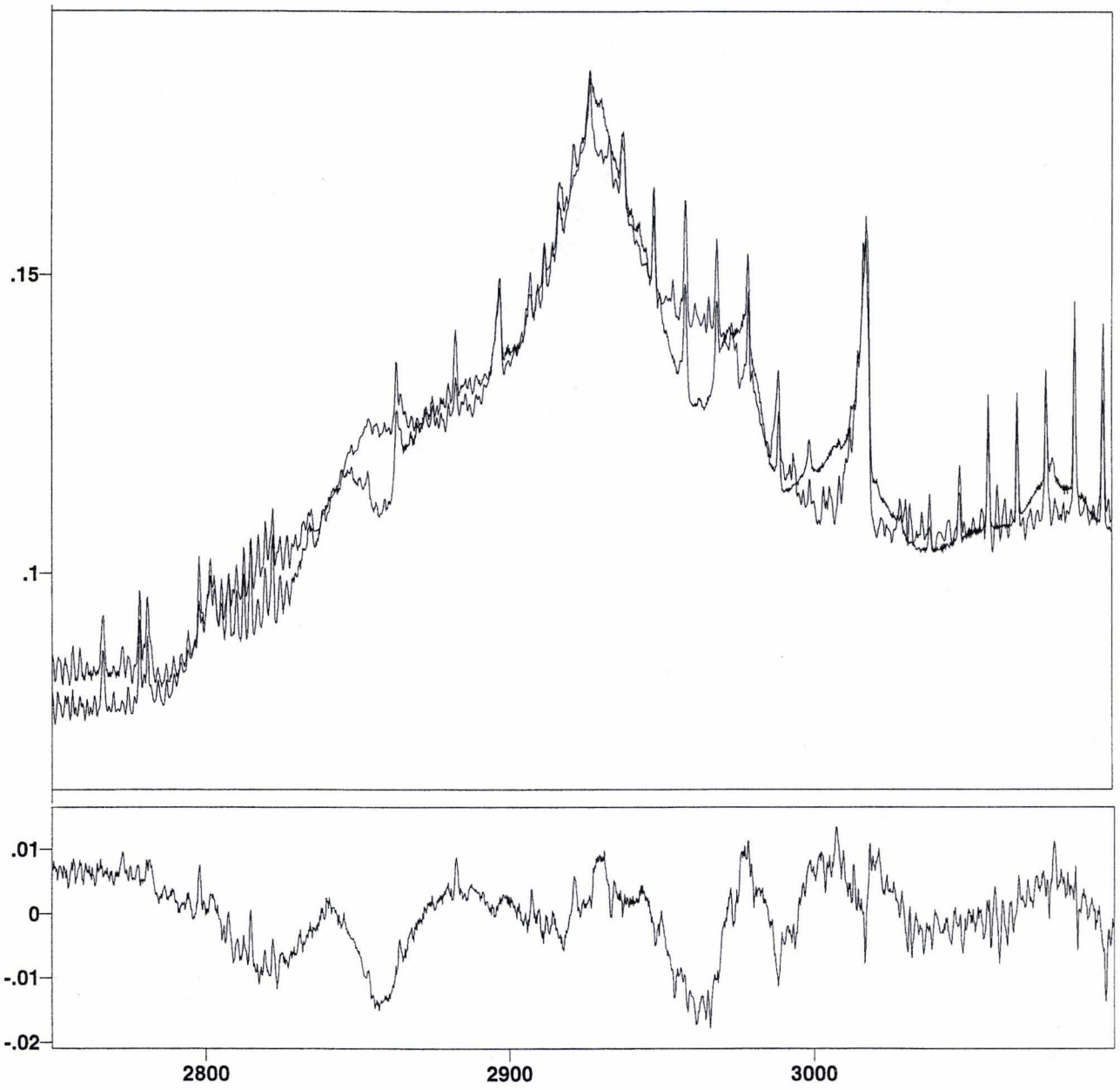

(b)
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Absorbance (base 10)
monoterpene mix
[Westberg et al., 1981]
smoke(sage)
3100
3050
3000
2950
2900
2850
2800
Wavenumber

Figure 3

KFIT v2.0 Spectrum: my24440i Calib: smol04t1 Fitted: 4/1/98 11:52 AM



1: a-pin : -.0381(.02260)

2: b-pin : .42090(.02581)

3: car : .50020(.02365)

4: lim : 1.3077(.03614)

5: myr : -.5892(.05177)

6: H2O : -.0026(.00481)

7: CH4 : .76459(.04326)

8: H2CO : .76461(.04256)

9: H2O-Q : -.0026(.00603)

10: CH4-Q : 3.7052(1.5330)

____ Measured

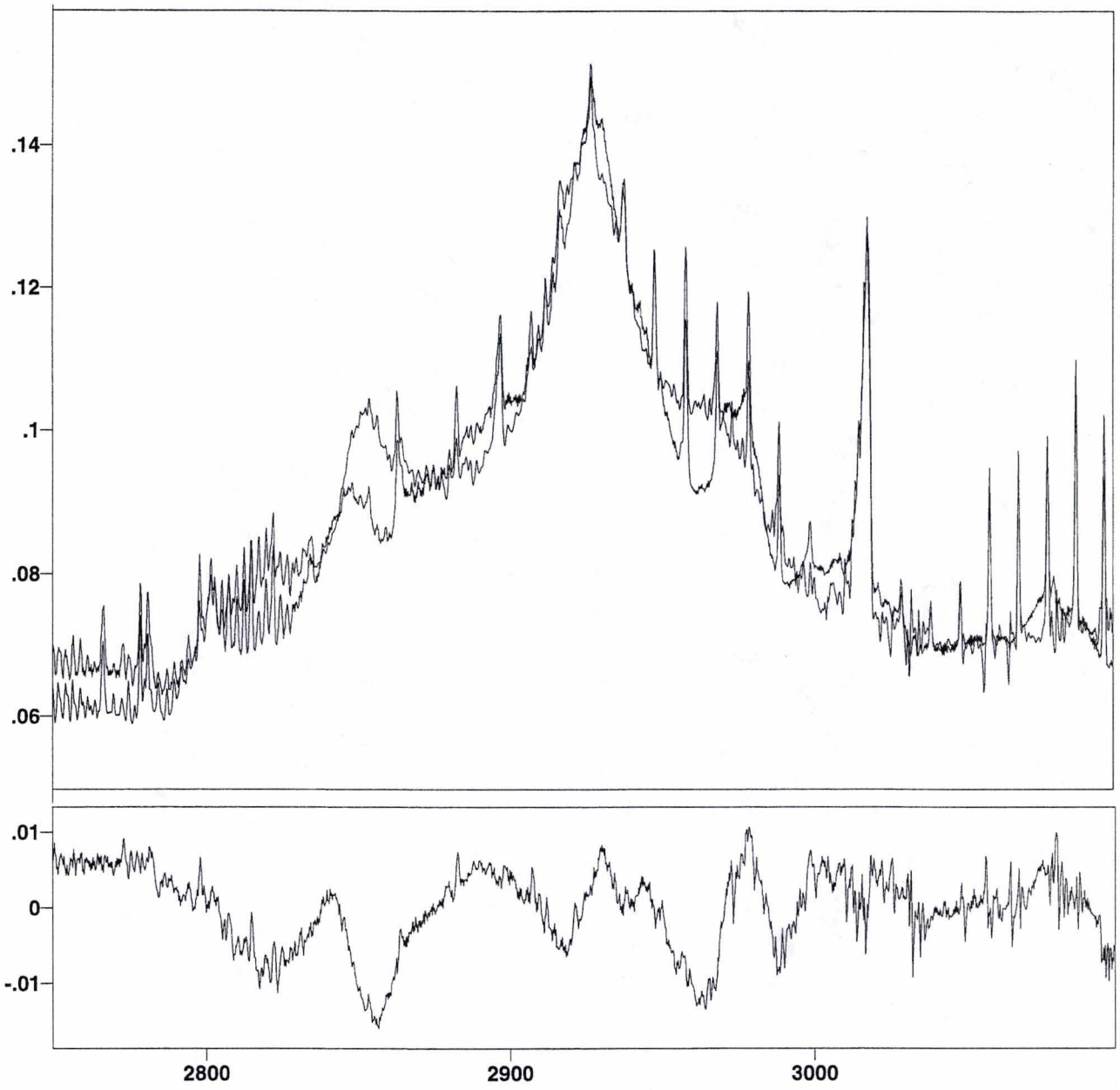
____ Fitted

____ Residual: RMS = .00572221588

Shift = none

T**2 Wt: No

KFIT v2.0 Spectrum: my20201i Calib: smol04t1 Fitted: 4/1/98 11:52 AM



1: a-pin : .08406(.02068)

2: b-pin : .32323(.02362)

3: car : .20173(.02165)

4: lim : 1.3030(.03307)

5: myr : -.6796(.04738)

6: H2O : -.0095(.00440)

7: CH4 : .95649(.03959)

8: H2CO : .71440(.03895)

9: H2O-Q : -.0076(.00551)

10: CH4-Q : 5.7991(1.4029)

____ Measured

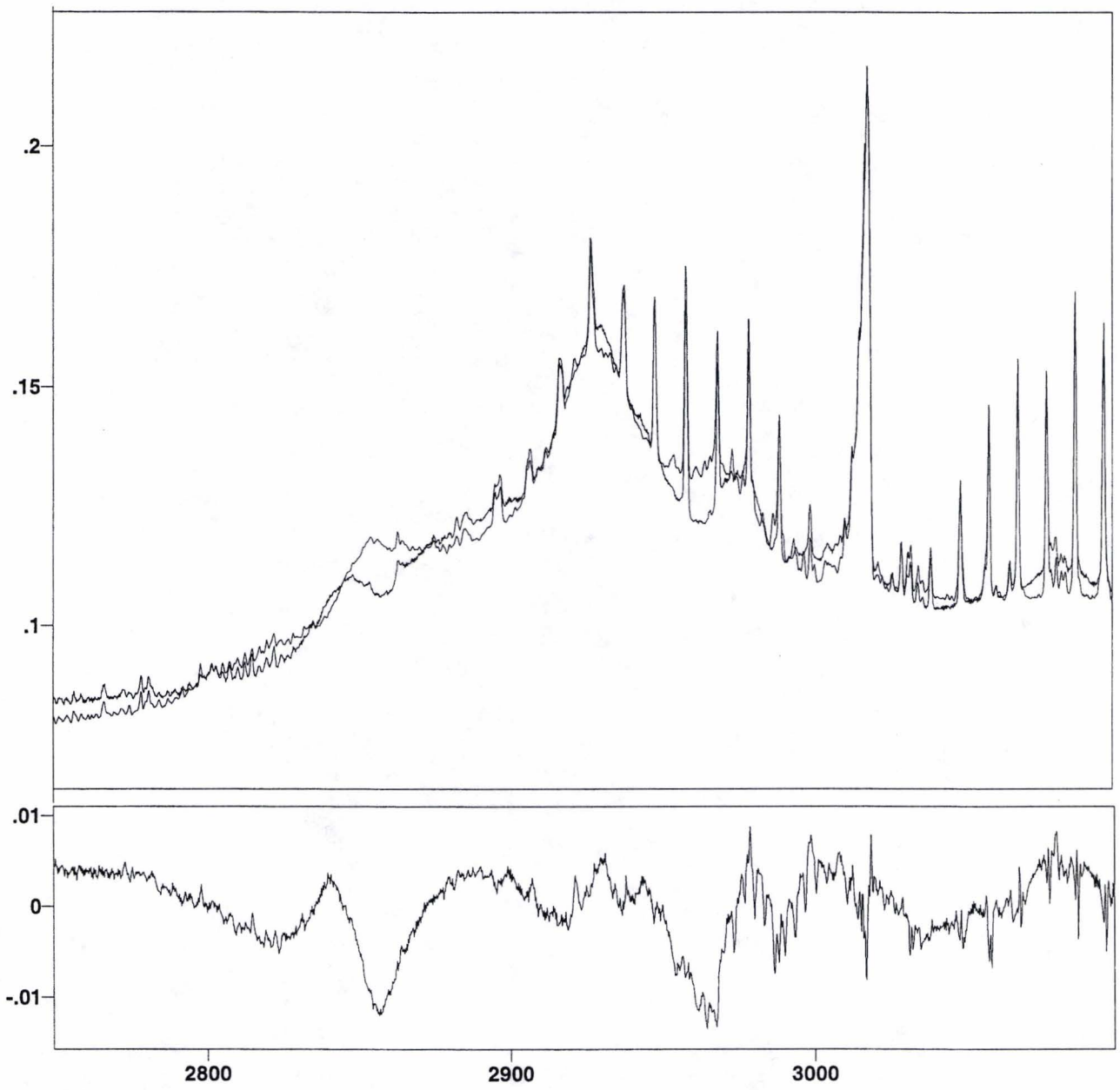
____ Fitted

____ Residual: RMS = .00523671903

Shift = none

T**2 Wt: No

KFIT v2.0 Spectrum: 011wfai Calib: smol04t1 Fitted: 4/1/98 11:55 AM



1: a-pin : .05048(.01556)

2: b-pin : .30919(.01777)

3: car : .25147(.01629)

4: lim : .91319(.02488)

5: myr : -.2987(.03565)

6: H2O : .01206(.00331)

7: CH4 : 2.0143(.02979)

8: H2CO : .22801(.02930)

9: H2O-Q : .00367(.00415)

10: CH4-Q : 16.834(1.0555)

____ Measured

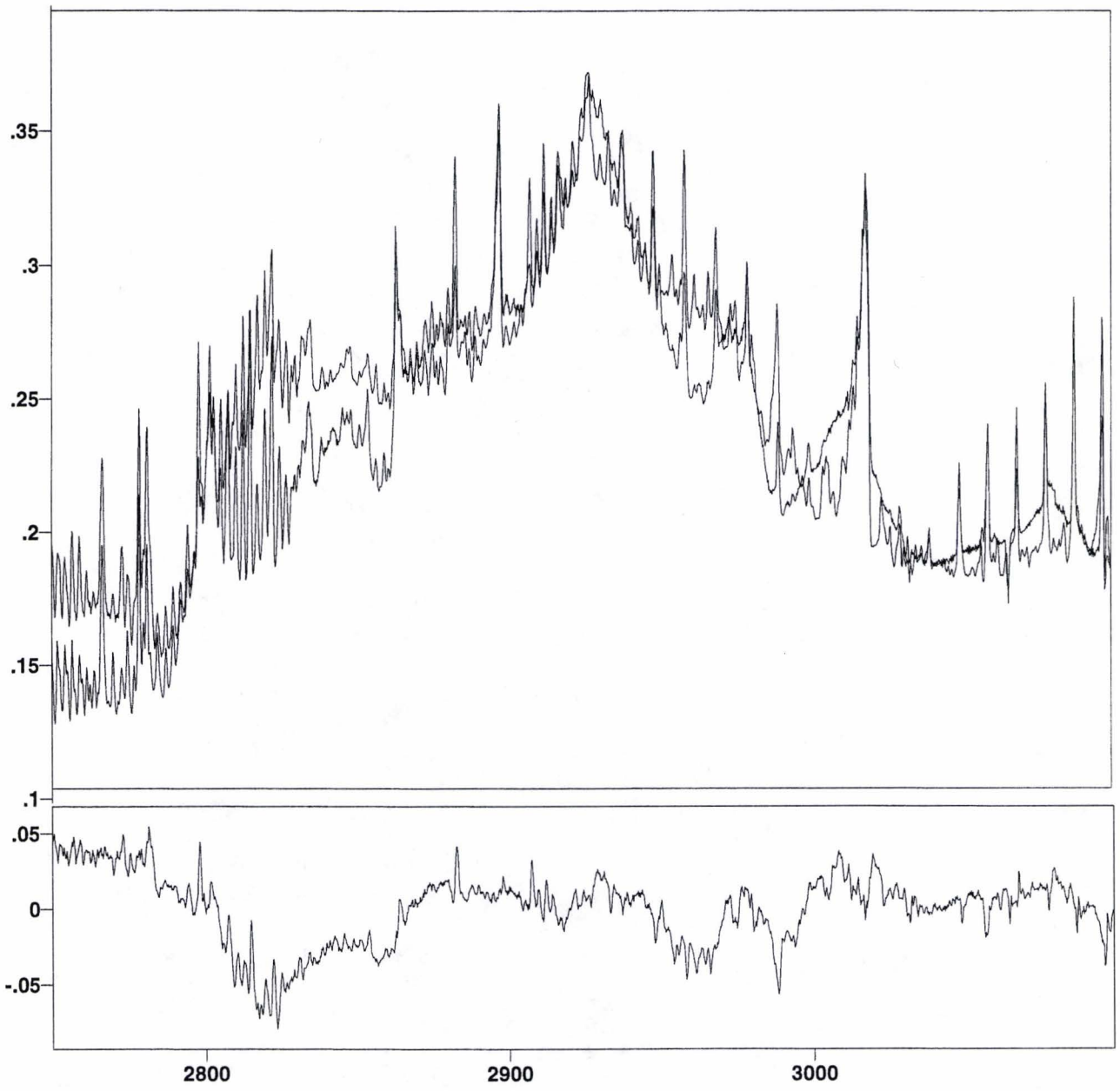
____ Fitted

____ Residual: RMS = .00394013864

Shift = none

T**2 Wt: No

KFIT v2.0 Spectrum: my22029i Calib: smol04t1 Fitted: 4/1/98 11:56 AM



1: a-pin : -.0424(.09273)

2: b-pin : .73130(.10590)

3: car : 1.8837(.09707)

4: lim : 2.8261(.14829)

5: myr : -1.768(.21246)

6: H2O : .03310(.01974)

7: CH4 : 1.8636(.17753)

8: H2CO : 4.4178(.17464)

9: H2O-Q : .05387(.02474)

10: CH4-Q : 7.9695(6.2904)

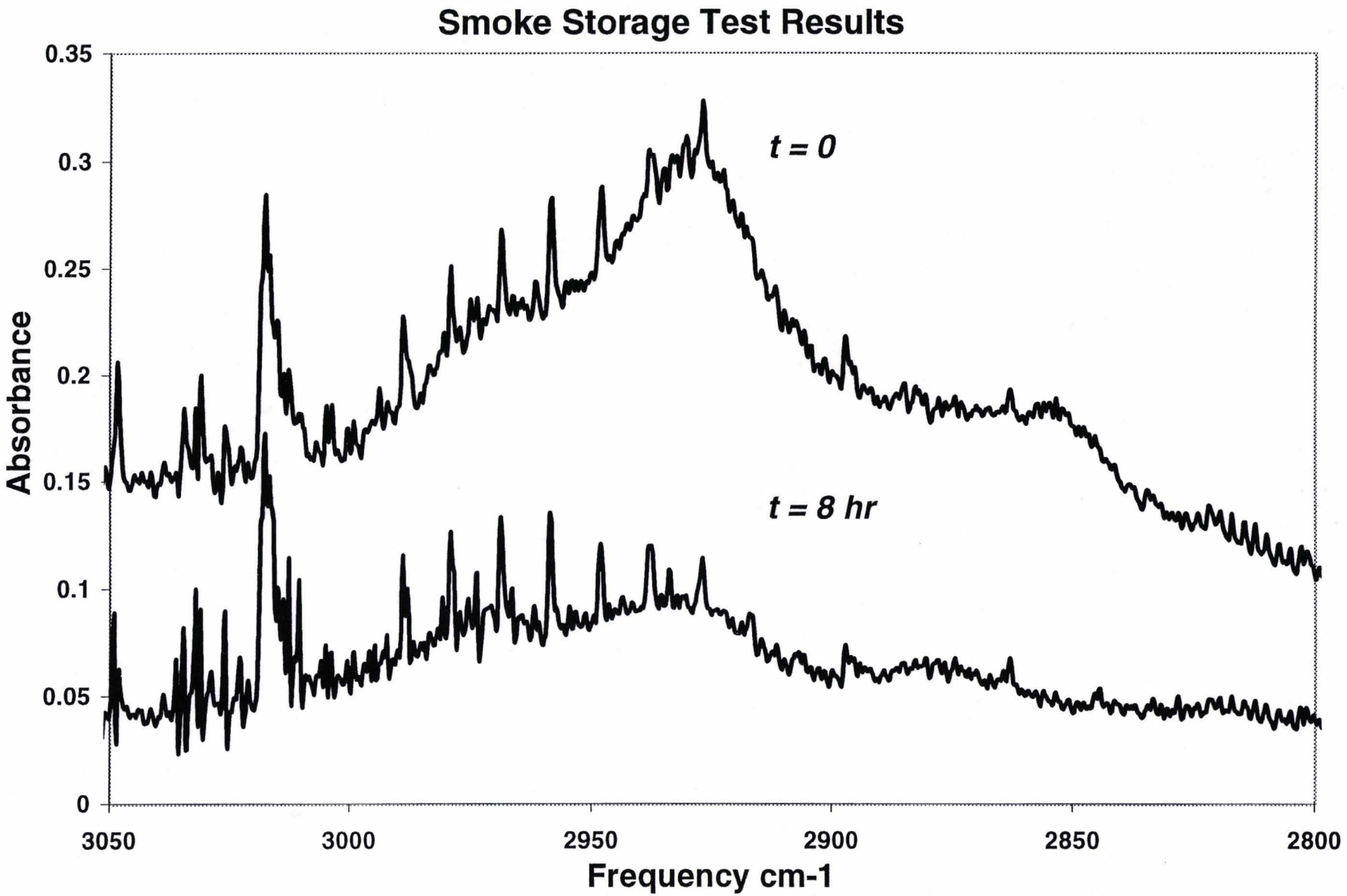
____ Measured

____ Fitted

____ Residual: RMS = .0234797731

Shift = none

T**2 Wt: No


Smoke Storage Test Results
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Absorbance
t = 0
t = 8 hr
3050
3000
2950
2900
2850
2800
Frequency cm-1